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Application of Thin Films of Conjugated Polymers in Novel Light-Emitting Devices and Liquid Crystal "Light Valves"

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Light-emitting electroluminescent diodes and electrochemically-driven electroluminescent devices involving conjugated polymers are described. The effect on the properties of polypyrrole films (deposited from aqueous polymerizing solutions of pyrrole) caused by the hydrophilicity/hydrophobicity of the substrate surface is utilized by a "microcontact printing" technique to form patterned liquid crystal display devices.

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APPLICATION OF THIN FILMS OF CONJUGATED POLYMERS IN NOVEL LIGHT-EMITTING DEVICES AND LIQUID CRYSTAL "LIGHT-VALVES"

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Abstract: Light-emitting electroluminescent diodes and electrochemically-driven electroluminscent devices involving conjugated polymers are described. The effect on the properties of polypyrrole films (deposited from aqueous polymerizing solutions of pyrrole) caused by the hydrophilicity/hydrophobicity of the substrate surface is utilized by a "microcontact printing" technique to form patterned liquid crystal display devices.

INTRODUCTION

The ability to cast high quality thin films of conducting polymers from their solutions in organic solvents (Ref. 1) or to deposit them on selected substrates from aqueous solution (Ref. 2) has permitted their use both in their lowly conducting (Ref. 3) and also in their highly conducting forms (Ref. 4) in novel devices. In this report, we describe the preparation and properties of certain types of the above films and their use in novel electroluminscent and liquid crystal display devices and in "microcontact printing".

RESULTS AND DISCUSSION

Symmetrically Configured AC Light-Emitting (SCALE) Devices

Light-emitting "5-layer" devices having the configuration M/EB/P/EB/ITO when M=Al, Cu or Au, EB=polyaniline (emeraldine base), P=poly(2,5-dihexadecanoxy phenylene vinylene pyridyl vinylene), PPV.PPyV and ITO=indium tin oxide glass show electroluminescent properties in both forward and reverse bias modes (Ref. 3). In order to understand the role of EB, the following devices were constructed in which the position and the number of layers of EB were varied from zero to one to two, viz., "3-layers":Al/PPV.PPyV/ITO; "4-layers-1": Al/PPV.PPyV/EB/ITO; "4-layers-2": Al/EB/PPV.PPyV/ITO; "5-layers": Al/EB/PPV.PPyV/EB/ITO. The corresponding I/V curves are given in Figure 1. Only the SCALE ("5-layers") device shows the capability of operating

in both forward and reverse bias modes and in an AC mode. A similar phenomenon is observed when copper is used instead of aluminum in analogous "3-layers" and "5-layers" devices. As can be seen, these devices exhibit most unusual electrical properties, viz., as the number of insulating layers *increases*, the total resistance of the device at a given potential *decreases*.

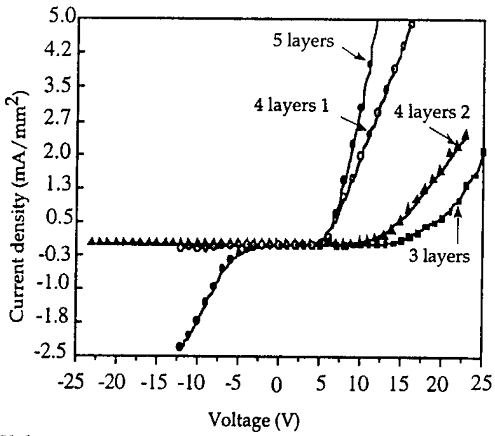

Fig. 1. I-V characteristics of 3-layered, 4-layered and 5-layered devices, (Ref. 3). Reproduced with permission of Elsevier Sciences, S. A., Lausane, Switzerland.

Electrochemically-Driven Light-Emitting Cells

Electrochemically-driven light-emitting cells have been described very recently although there is not yet complete agreement as to the exact mechanism or processes by which they operate (Ref. 5). It has been reported (Ref. 5) that if the polyethylene oxide, PEO, is eliminated from a Al/PPV;$LiCF_3SO_3$;PEO/ITO cell where PPV=poly(*p*-phenylene vinylene) that it behaves similarly to the conventional Al/PPV/ITO LED device. However, we find that in an Al/MEH-PPV;TBATS/ITO cell where MEH-PPV=poly(2-methoxy-5-(2'-ethyl-hexoxy)-1,4-phenylene-vinylene and TBATS=tetrabutylammonium p-toluenesulfonate (Figure 2) that it behaves very differently from an Al/MEH-PPV/ITO device. In particular, the presence of TBATS: (i) involves light-emission in the reverse bias mode, (ii) results in a much greater light intensity clearly visible in the presence of a direct overhead fluorescent light, (iii) results in a lower turn on voltage and (iv) that in some, but not all devices, the current is in the microampere range rather than in the milliampere range normally associated with a conventional LED. We believe that such devices are of very great scientific interest and of potential technological importance.

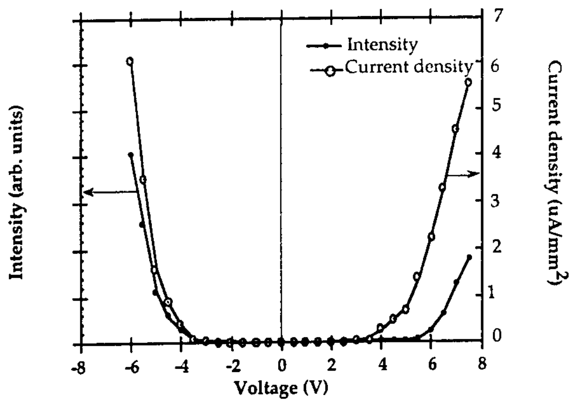

Fig. 2. Current density and intensity of light emission vs voltage in a Al/MEH-PPV+TBATS/ITO device, (Ref. 6). Reproduced with permission of the Materials Research Society, Pittsburgh, PA.

"1-Dip" *in situ* Deposition of Polypyrrole and Polyaniline on Hydrophobic and Hydrophilic Glass Surfaces.

High quality thin films of doped polypyrrole and doped polyaniline can be conveniently deposited during a few minutes at room temperature on glass and plastic substrates from dilute aqueous solutions of the respective monomer as it undergoes oxidative polymerization (Ref. 2) by an *in situ*, "1-dip" process. We find that the deposition rate and the properties of the films are greatly dependent on the nature of the substrate surface, e.g., whether deposited on hydrophilic surfaces or surfaces rendered hydrophobic by treatment with $C_{18}H_{37}SiCl_3$ as shown in Figure 3.

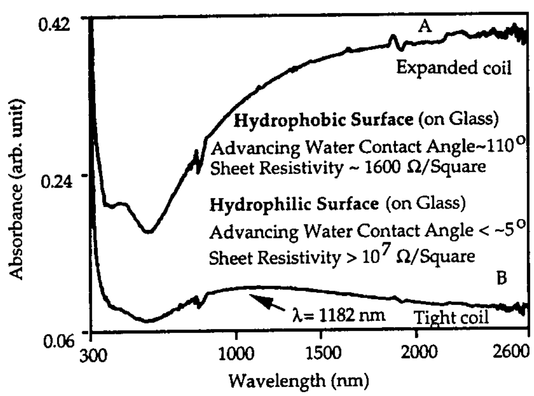

Fig. 3. Vis/uv spectra of polypyrrole anthraquinone-2-sulfonate deposited (dipping time: 15 minutes) on (A) a hydrophobic glass surface (film thickness ~ 400 Å) and (B) a hydrophilic glass surface. (Spectrum A was recorded vs. a hydrophobic glass slide in the spectrometer reference beam and spectrum B was recorded vs. a hydrophilic glass slide in the spectrometer reference beam), (Ref. 8).

This figure shows the results of deposition studies involving polypyrrole (Ref. 6) in which a hydrophilic and a hydrophobic glass microscope slide were dipped in the same solution of polymerizing pyrrole for 15 minutes. The rate of deposition of polymer on the hydrophobic surface is very much greater than on the hydrophilic surface.

Not surprisingly, the surface resistance of the thinner films on the hydrophilic surfaces is very much greater than that of the thicker films deposited on the hydrophobic surfaces. As can be seen from Figure 3, the spectra of the polypyrrole films deposited on hydrophilic and hydrophobic surfaces differ greatly. By analogy with studies on polyaniline (Ref. 7), we believe that the polymer deposited on the hydrophilic surface might have a tight coil molecular conformation while that deposited on the hydrophobic surface might have an expanded coil molecular conformation.

Flexible Liquid Crystal "Light Valves"

Novel, flexible, completely organic, polymer dispersed liquid crystal (PDLC) "light valves" were fabricated using two flat pieces of commercial overhead transparency substrates coated with polypyrrole by the *in situ*, "1-dip" process between which a film of commercial PDLC material was sandwiched. For use in flat screen liquid crystal displays it is necessary to optimize the thickness of the polypyrrole deposit so as to simultaneously obtain the maximum transmittance and minimum resistance necessary for satisfactory devices. Figure 4 gives preliminary results obtained to date with a completely flexible, all organic light valve using polypyrrole as the conducting medium for both electrodes (Ref. 6). A PDLC device using conducting ITO glass for both electrodes was used as a standard for comparison. The results are satisfactory for certain applications such as light-weight, non-breakable windows of variable transmittance.

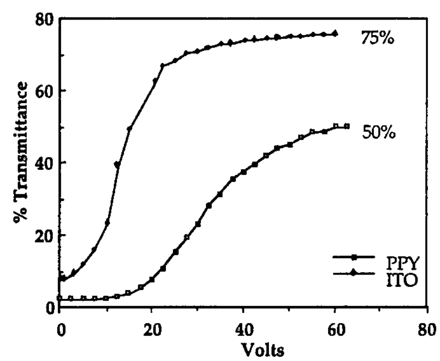

Fig. 4. Relationship between transparency (% transmittance in air at 600 nm) and applied voltage of polymer dispersed liquid crystal display devices constructed using two ITO glass electrodes and two polypyrrole film (on plastic) electrodes as the conducting transparent substrates. (Ref. 6) Reproduced with permission of the Materials Research Society, Pittsburgh, PA.

Application of "Microcontact Printing" for the Production of Patterned Polypyrrole and Polyaniline Films

We have combined the selective deposition of polypyrrole on hydrophilic/hydrophobic surfaces as described in the preceeding section with the recent discovery of the microcontact printing technique (Ref. 9) to produce patterned conducting polymer films which we have demonstrated can be used in PDLC display-type devices. The steps comprise: (i) designing any desired pattern on the computer, (ii) reducing the pattern on the computer to any desired size, e.g. > ~ 1 cm x 1cm, (iii) replacing the pen in the plotter of a common laboratory spectrometer by an object with a sharp point, e.g. a sewing needle, (iv) scratching the pattern on a thin layer of wax using the needle in the pen holder of the plotter, (v) making a silicone elastomeric stamp from the wax engraving, (vi) wiping the patterned face of the silicone stamp with an "ink" solution of $C_{18}H_{37}SiCl_3$, (vii) pressing the stamp firmly on the substrate surface so as to imprint a pattern of a thin hydrophobic $C_{18}H_{37}$- film on the substrate, (viii) placing the substrate having the imprinted $C_{18}H_{37}$- layer into an aqueous polymerizing pyrrole or aniline solution.

Examples of the selectivity of a polypyrrole "1-dip", *in situ*, deposition are given in the SEM's in Figure 5. Dark lines are polypyrrole selectively deposited on hydrophobic $C_{18}H_{37}$- surfaces imprinted on a clean, hydrophilic microscope slide as substrate. The upper three figures (Figures 5a) originated from a desk-top computer-drawn pattern used for producing the wax engraved master; the deposition time in the polymerizing pyrrole solution was 12.0 min. The lower two figures (Figures 5b) demonstrate the resolution attainable using a commercial relief master from which the silicone stamp was made. Since the silicone stamps can be used repeatedly without loss of resolution (Ref. 9), this technique holds potential promise for the inexpensive production of semi-micro circuitry and liquid crystal displays on rigid or flexible substrates in certain types of "throw away" devices such as, e.g., sensors.

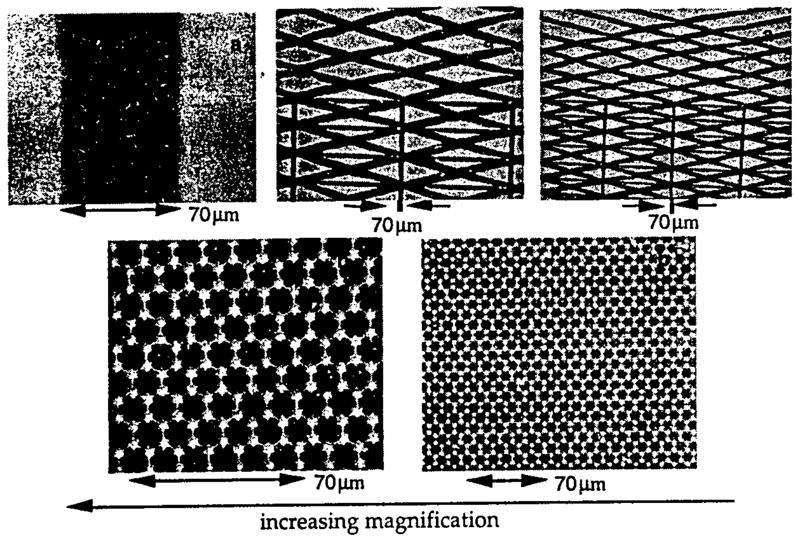

Fig. 5. Selective deposition of polypyrrole on patterned hydrophobic surfaces, (Ref. 8).

An effective polymer dispersed liquid crystal interdigitated array display has been fabricated by combining the concepts and techniques given in the preceeding sections.

CONCLUSIONS

It is concluded that : (i) the role of electrode/polymer and polymer/polymer interfaces is of critical importance in LED devices; (ii) light-emitting electrochemical cells are of significant potential technological importance but are as yet, little understood and (iii) the nature of substrate surfaces greatly affect the properties of conducting polymers deposited upon them; the phenomenon can usefully be exploited in microcontact printing.

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